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FINAL TECHNICAL REPORT
RESEARCH ON SOLID-PROPELLANT COMBUSTION

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January 31, 1962

Director of Aeronautical Sciences
Air Force Office of Scientific Research
Washington 25, D. C.

ATTN: SRHP

Subject: Final Technical Report AFOSR 2005 (Contract AF 49(638)-813)
"Research on Solid Propellant Combustion."

Dear Sir:

I enclose a copy of the subject report, which you have approved for distribution. Other copies are being mailed in accordance with the distribution list on pages 27-28 of the report.

Sincerely,

ATLANTIC RESEARCH CORPORATION

Raymond Friedman, Director
Kinetics and Combustion Division

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AFOSR 2005

CONTRACT AF 49(638)-813

FINAL TECHNICAL REPORT

RESEARCH ON SOLID-PROPELLANT COMBUSTION

TO:

Propulsion Research Division
Air Force Office of Scientific Research
Office of Aerospace Research
United States Air Force
Washington 25, D. C.

FROM:

Kinetics and Combustion Division
Atlantic Research Corporation
Alexandria, Virginia
December 31, 1961

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I. INTRODUCTION

In 1955, Atlantic Research Corporation, under Air Force Office of Scientific Research sponsorship, initiated a program of research on the mechanism of combustion of solid propellants, with emphasis on ammonium perchlorate-based systems. Continuity in this research effort has been maintained from 1955 to the present time by virtue of support under Contract AF 18(600)-1502 and under the present Contract AF 49(638)-813. During the two contracts, five Technical Notes have been written (1, 2, 3, 4, 5). Formal papers have been presented at the Sixth International Symposium on Combustion, the Eighth International Symposium on Combustion, the September 1961 National Meeting of the American Chemical Society, and the Fifteenth Joint Army-Navy-Air Force Solid Propellant Group Meeting, 1959. In addition, less formal talks have been given at annual Air Force Office of Scientific Research contractors' meetings and by invitation at various universities and research institutions. Direct contact has also been maintained with other research groups making parallel attacks on the same problem area, including Nachbar at Lockheed, Summerfield et al. at Princeton, and Schultz, Chaiken, Andersen, et al. at Aerojet-General Corporation.

Previous reports originating from this project (1, 2, 3, 4, 5) have emphasized the finding, apparently first reported by Adams, Newman, and Robins (6), that a flame will propagate through pure ammonium perchlorate at rates comparable with composite solid-propellant burning rates at elevated ambient pressures. Thus, attention has been concentrated on study of the ammonium perchlorate combustion mechanism in the absence of organic or metallic fuel, on the assumption that, at least under some conditions, the ammonium perchlorate decomposition flame is rate-controlling in composite propellants. The most recent publications of Summerfield et al. (7) as well as Vandenkerckhove and Jaumotte (8), concur that this is the case at pressures above about 50 atmospheres. (The evidence will be discussed in detail in Section IV of this report.)

The experimental work already carried out and reported in this program includes measurements of burning rate and lower pressure limit of flammability of dead-pressed ammonium perchlorate as a function of ambient pressure, initial

temperature, incident radiant flux, and catalyst content. Temperature measurements have been made with fine thermocouples and by photopyrometry. Detailed chemical analysis of combustion products has been carried out for a variety of combustion conditions. Kinetics of the gaseous decomposition of perchloric acid vapor has been studied. In very recent and incomplete work reported in Section II, experiments dealing with kinetics of the perchloric acid vapor-ammonia reaction are presented. In Section III, a variety of experiments dealing with pure ammonium perchlorate deflagration and interactions of deflagrating ammonium perchlorate with gaseous and solid fuels in controlled geometries are described.

In addition to this body of experimental work, much thought has been given to the coupling of the various rate processes and to possible kinetic schemes relevant to the governing chemical reactions. Simplified mathematical models have been developed, and the more accurate model developed by Nachbar, which however, requires extensive computation to obtain numerical solutions, has been carefully considered. Attention has been given to experimental results arising out of other programs, such as Aerojet's hot-plate pyrolysis work and Princeton's measurements of burning characteristics of organic fuel-ammonium perchlorate mixtures. In Section IV, a review is presented of our current understanding of the combustion mechanism of ammonium perchlorate-based solid propellants, with emphasis on our own work but with consideration to the work of others also.

Much progress has occurred in our understanding of this complex rate process in the past several years. This may be helpful to those seeking to develop a theory of the interaction between an acoustic wave and a burning solid propellant, for example. However, it must be said that the last word has not yet been written on ammonium perchlorate, and further research is still required to give a complete picture of the burning mechanism.

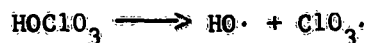
II. RECENT EXPERIMENTS WITH AMMONIA AND PERCHLORIC ACID VAPOR

Since the postulate that ammonia and perchloric acid are vaporized from the ammonium perchlorate surface and react exothermally above it seems

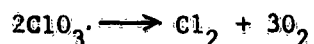
inherently so reasonable, it was a logical extension of the present research to investigate the nature of the chemical reactions that would occur with these species.

The basic alternative reaction paths that are possible for this system are that: (a) the perchloric acid could decompose first and its decomposition products, which could include chlorine, oxygen and the oxides of chlorine, could then oxidize the ammonia; or (b) perchloric acid could react with ammonia directly. A decision could be reached between these two alternatives by a kinetic study of the thermal decomposition of perchloric acid alone and then in the presence of ammonia. In the present program it has been possible only to complete the study for perchloric acid alone* and to conduct a limited number of experiments with added ammonia. These results are discussed below.

The thermal decomposition of perchloric acid vapor is complicated by the fact that the reaction, when studied in glass vessels, has a large heterogeneous contribution at temperatures below about 315°C. Above this temperature the reaction kinetics are those of a homogeneous reaction. The reaction was studied by a colorimetric technique from 200-350°C and by a flow method from 350-439°C. The data from 200-315°C were quite scattered because of the heterogeneous nature of the reaction and the difficulty of reproducing unknown surface conditions. The Arrhenius curve was quite flat, indicating an activation energy of about 10 or 15 kcal/mole. The homogeneous reaction data was quite good and yielded the rate expression $k = 5.8 \times 10^{13} \exp(-45,100/RT) \text{sec}^{-1}$. The 45 kcal activation energy is very close to the O-Cl bond strength and indicates that the rate-determining step in the reaction is



A mechanism has been proposed in which this step is followed by



*This work has been described in AFOSR TN 1555, October 1961.

The products indicated, chlorine, oxygen, and water, are those experimentally observed over the entire temperature range.

Experiments with ammonia have been performed at 367°C. Essentially, the experiments involve the preparation of separate streams of nitrogen-ammonia and nitrogen-perchloric acid mixtures, the mixing of these streams and their passage through a reaction vessel at a fixed temperature. The products emerging from the reaction vessel were then absorbed in a series of traps. Analyses were performed for chloride (no hypochlorite was found) and perchlorate ion. The initial ammonia concentration was known from the composition of the ammonia-nitrogen stream and the flow rates.

The principal problem was that of mixing the two reactants completely in a time short compared to the reaction time. The results of the experiments at 367°C are summarized in Table I.

Table I

The Rate of Reaction of Perchloric Acid in the Presence of Ammonia at 367°C

Run	Initial Concentrations in moles/liter x 10 ³		Reaction Time (sec.)	Percent Decomp. of		k_2 Obs. (cm ³ moles ⁻¹ sec ⁻¹)
				HC1O ₄ Calc. for HC1O ₄ Alone		
1	NH ₃ 8.14	HC1O ₄ 3.04	1.96	3.5	16.7	0.29 x 10 ⁶
2	21.0	2.80	1.96	3.5	43.8	1.38 x 10 ⁶
3	7.15	1.92	1.99	3.5	26.9	1.82 x 10 ⁶
4	16.0	3.05	3.64	6.0	66.0	2.20 x 10 ⁶

It is clear from the increased per cent reaction in the presence of ammonia that reaction is occurring between perchloric acid and ammonia as well as by direct decomposition of the former. The last column of the table lists values obtained for the rate constant for the ammonia-perchloric acid reaction. These values were calculated from the kinetic expression

$$\frac{-d\text{HC1O}_4}{dt} = k_1 \text{HC1O}_4 + k_2 (\text{HC1O}_4)(\text{NH}_3)$$

This involves the assumption that the acid-ammonia reaction is first order in each reactant. Since only these few preliminary data could be obtained, the kinetics of the reaction remain in question, but the calculation of k_2 serves as a method to examine the data that were obtained. In order to make the calculation of the rate constants it was necessary to assume a stoichiometry of the reaction. Since the deflagration of ammonium perchlorate at atmospheric pressure yields chlorine as a product (4), and since only chloride was found in these experiments, it has been assumed that two ammonia molecules are consumed for each perchloric acid molecule decomposed, i.e., that chlorine is the product of reaction of one ammonia with perchloric acid and that a second ammonia reacts with the chlorine to give chloride.

In runs 1 and 2 above, the mixing chamber used was designed after that described by Johnston and Yost (9) in their study of the ozone-nitrogen dioxide reaction. In runs 3 and 4 two such mixers in series were used. The relatively good agreement of the latter two runs indicates that mixing was quite efficient in those cases and that the rate constant of about $2 \times 10^6 \text{ cm}^3 \text{ moles}^{-1} \text{ sec}^{-1}$ is correct for this temperature. This result must, however, be confirmed by further work.

It is of some interest to estimate the value of k_2 at the flame temperature of ammonium perchlorate, i.e., 1200°K (1). This may be done taking the above rate constant and assuming different energies of activation. From this constant and the value of k_1 at 1200°K , $3.7 \times 10^5 \text{ sec}^{-1}$, the ratio of the first order contribution to that of the second order, i.e., $k_1/k_2 P$ can be evaluated.* The relevant data are shown in Table 2.

Table 2

The Effect of Activation Energy and Pressure on the Relative Importance of Uni- and Bimolecular Mechanisms at 1200°K

$E_{\text{act.}}$ (kcal/mole)	k_2 ($\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$)	$r = k_1/k_2 P$ for P equal		
		<u>5</u>	<u>25</u>	<u>50</u> atm
10	1.6×10^8	46	9.2	4.6
20	6.2×10^9	1.17	0.23	0.12
30	2.5×10^{11}	0.03	0.006	0.003

*It is assumed that ammonia and perchloric acid are present at equal pressures, P .

Thus it is clear that if the energy of activation of the bimolecular reaction is about 20 kcal/mole both mechanisms would be important over the pressure range of interest. If the energy of activation is much lower than this figure the unimolecular mechanism would be predominant while if it is higher the bimolecular mechanism prevails.

The observation that solid was deposited in the mixing chambers for certain flow conditions gave a crude measure of the vapor pressure of ammonium perchlorate. Thus it was found that when the partial pressures of ammonia and perchloric acid were 2.2×10^{-3} atm. and 1.78×10^{-3} atm., a deposit was observed in the mixing chambers at 362°C but not at 367°C . If the equilibrium constant for vaporization is defined as $K = \frac{P_{\text{NH}_3}}{P_{\text{HClO}_4}}$, then at about 367°C this constant has the value 3.9×10^{-6} atm².

An interesting calculation can be made using this figure if it is assumed that the standard entropy of vaporization of ammonium perchlorate can be approximated by that of ammonium chloride, $\Delta S^\circ = 68 \text{ cal mole}^{-1} \text{ deg.}^{-1}$ (10). Then $\Delta H = 68T$ where T is the temperature at which the vapor and the solid are in equilibrium and are all at one atmosphere, and from the Clausius-Clapeyron equation

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{3.9 \times 10^{-6}}{1} = \frac{68T}{R} \left(\frac{1}{T} - \frac{1}{640} \right)$$

This expression yields $T = 878^\circ\text{K}$ and $\Delta H = 59.5 \text{ kcal/mole}$. This value of ΔH is fairly close to that calculated for the process $\text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_3(\text{g}) + \text{HClO}_4(\text{g})$ (11), i.e., 56,000 cal/mole. Since the assumed entropy was that of an ammonium salt that dissociates on vaporizing, the results are internally consistent in supporting the view that ammonium perchlorate is dissociated in the vapor phase.

III. RECENT EXPERIMENTS ON AMMONIUM PERCHLORATE AND POTASSIUM PERCHLORATE DEFLAGRATION

This section of the report will review those experimental results not already described in previous publications (1, 2, 3, 4, 5). These are for the most part relatively recent and in some cases incomplete results.

A. Pressure Limit of Flammability

Previously reported experiments showed that dead-pressed strands of pure ammonium perchlorate of 4 x 4 mm cross-section would propagate a flame downward when ignited with an energetic propellant mixture containing aluminum, as long as the ambient pressure was greater than 22 atm. In order to determine if the heat losses which may be governing this limit are radiative or convective in nature, experiments have now been conducted with substantially larger pressed strands. These were pressed in a steel mold having a cylindrical cavity of 25-mm diameter and 38-mm depth. The "strands" were ignited without removal from the mold.

Complete burning was observed with these strands at pressures of 19.7 atm and above. The flame did not propagate at 18.4 atm and below. The 22-atm limit previously observed with the 4-mm strands had not been determined with high precision. In view of the relative insensitivity of the limit to diameter, it is felt that radiative loss is the dominant mode of loss.

B. Effects of Preheating on Combustion of Ammonium Perchlorate

The previous work has shown that ammonium perchlorate initially at room temperature will not support a decomposition flame except with an incident radiant flux of at least $10 \text{ cal/cm}^2\text{-sec}$. However, other experiments have now shown that atmospheric-pressure combustion can be attained by uniformly preheating the strand to about 270-280°C. Burning rates at atmospheric pressure were measured as follows:

Initial Temperature (°C)	Burning Rate (cm/sec)
248	Failed to propagate
250	" " "
262	" " "

Cont'd	Initial Temperature (°C)	Burning Rate
	269	0.029
	275	0.027
	317	0.027
	322	0.032

These rates are seen to be very close to the value of 0.025 cm/sec obtained with an incident radiant flux of about 15 cal/cm²-sec.

C. Interactions of Deflagrating Ammonium Perchlorate with Methane

The investigators at Waltham Abbey have observed that a diffusion flame can be established around a piece of ammonium perchlorate in a stagnant fuel-gas atmosphere, even at subatmospheric pressure. We have done exploratory experiments involving flowing methane and various controlled geometries, described below, at one atmosphere.

One geometry of interest involves a methane jet issuing from a convergent nozzle of 9.5 mm diameter, impinging on an ammonium perchlorate strand of 4 x 4 mm cross-section, which is being fed through a square hole in a flat plate so that the burning surface remains in the plane of the flat plate. A jet stand-off distance of 12.7 mm was used in a set of tests to be described below. Ammonium perchlorate regression rate could be measured as a function of jet velocity.

Methane Velocity (cm/sec)	Strand Regression Rate (cm/sec)
280	0.023
400	0.031
631	0.046
1093	0.051
1555	0.051
2480	0.052

The regression rate is seen to become independent of gas flow rate above about 1000 cm/sec. Similar behavior was observed with strands containing three per cent copper chromite catalyst except that the asymptotic rate was

0.085 cm/sec instead of 0.051 cm/sec.

Visual observation shows a blue gaseous flame with a yellow cap on the methane side, just above the perchlorate surface. The yellowness of the cap increases with increasing methane velocity. For the copper chromite-containing strands, there was no yellow cap, surprisingly, but only an intense blue-violet flame.

No flame blowout could be obtained by increasing the flow velocity even to 25000 cm/sec with the geometry described above, even though theoretical arguments put forth by D. B. Spalding suggest that a critical velocity must exist above which extinction occurs because the chemical reaction rate becomes overshadowed by the cooling effect of the arriving methane. (Such an effect, if it could be observed, would provide valuable information on the overall kinetics of the propellant flame.) Flame extinction could be induced by using a sufficiently dilute methane-nitrogen mixture instead of pure methane, but when the stability limit diagram (jet composition vs critical jet velocity) was determined, it was found that flame-out occurs on dilution to about 20 mole per cent methane in nitrogen virtually regardless of flow velocity. Clearly, such high dilution has produced nonflammable mixtures, and the flame-out is due to composition change rather than velocity.

In other experiments with a different geometry, flame-out could be observed in pure methane jets. In this case, the side-shielding of the flat plate was not employed, but the strand of ammonium perchlorate was held in the free methane jet, the strand aligned along the axis of the jet. On igniting with a torch at relatively low methane velocity, a flame-cap formed over the "nose" of the specimen, sculpturing it from rectangular to needle-shaped. At this point, methane velocity was increased to the maximum available (2500 cm/sec), upon which the flame-cap at the nose of the specimen disappeared, although a flame was visible a few mm downstream of the nose, in a region where the boundary layer had built up somewhat. Precise measurements of flame stability were not made with this setup because the specimen shape was changing with time. However, such experiments could probably be fruitfully pursued, if high-speed photography was utilized.

Yet another geometry was employed in a new series of experiments. An axial hole was drilled through a pressed strand, through which methane was allowed to flow upward at controlled velocity. The emerging methane jet was ignited, and subsequent phenomena observed as a function of hole diameter and methane velocity. For a 0.66-mm hole diameter, the surface regression rate of the strand was about 0.025 cm/sec, independent of flow velocity from a few cm/sec up to 130 cm/sec. In a test at 250 cm/sec, the flame became unstable and blow-out occurred. For a 1.6-mm hole, the regression rate was again independent of flow rate but was larger, about 0.04 cm/sec. Extinction occurred rather than flashback when the methane flow was cut off. Experiments were then made with a much larger square hole, 5 x 5 mm, formed by gluing four pressed pieces of ammonium perchlorate together, to see if flashback into the hole could occur at a very low flow rate. However, only steady propagation into the hole at about 0.2 cm/sec occurred, and the flame went out when the methane flow was interrupted. It was concluded from these tests that the methane diffusion flame can preheat the perchlorate sufficiently to allow the perchlorate decomposition flame to propagate; but no quantitative measure of the interaction could be attained.

Spalding (13) has made a theoretical mass-transfer analysis of the interaction of a methane jet with an ammonium perchlorate diffusion flame, and he concluded that the burning rate was controlled primarily by the deflagration characteristics of the ammonium perchlorate, the effect of the boundary-layer induced enthalpy gradient associated with methane combustion being very small. However, since the perchlorate will not burn at all at one atmosphere if the methane flame is not present, he proposes that a radiant interaction not included in his treatment may become important at low ratios of methane to perchlorate.

D. Interactions of Deflagrating Ammonium Perchlorate with a Polymer

When a ground crystalline oxidizer such as ammonium perchlorate is mixed with an organic binder which is then polymerized, the resulting geometry is exceedingly complex. More important, each pocket of oxidizer or fuel in the heterogeneous material burns in an unsteady-state mode as the flame reaches it. Thus, a simpler geometry which might give a steady-state polymer-oxidizer

interaction is of research interest. One possibility, which we have explored, is to drill an axial hole in a pressed strand of ammonium perchlorate and fill it with an organic liquid which is then polymerized. The strand would then be ignited so as to burn in the direction of the hole axis.

In preliminary experiments, strands were drilled and the hole filled with liquid dioctyl adipate. The strands were ignited at atmospheric pressure with an incident radiant source of $15 \text{ cal/cm}^2\text{-sec}$. The liquid was observed to boil from the hole presumably by heat transfer from the hot surrounding perchlorate. It was decided to conduct further tests with a polymerizable liquid.

A liquid was prepared consisting of 2/7 dioctyl adipate (by wt) and 5/7 polyvinyl chloride microspheres (plastisol grade). This liquid could be injected into small drilled holes in a pressed strand with a hypodermic needle, and then solidified by heating at 120°C for one hour and then cooling. A process of solution rather than polymerization occurs in this case. In experiments with 685-micron holes filled with the above plasticized polyvinyl chloride, combustion at one atmosphere was achieved with an incident radiant flux of $15 \text{ cal/cm}^2\text{-sec}$. The propagation rate of strands with such an axial polymer column averaged 0.031 cm/sec while the pure ammonium perchlorate strands averaged 0.022 cm/sec. On interrupting the burning, the perchlorate surface was observed to be a concave cone with half-angle roughly 45° . Interpretation of such experiments is difficult because the radiation-absorption properties of the partially carbonized polymer may make an important contribution. Evidence of char formation was seen in these interrupted-burning tests.

Therefore, the radiation flux was eliminated and combustion of strands containing polymer filaments was carried out in a bomb at elevated pressure.

Results were as follows:

660-micron holes: burning rate similar to that of matrix (pure ammonium perchlorate) in the range from 20 to 45 atm, but substantially greater than the matrix at higher pressures (40 per cent higher at 140 atm).

500-micron holes: burning rate unchanged from matrix rate over entire range from 20 to 140 atm.

340-micron holes: burning rate unchanged from matrix rate of entire range from 20 to 140 atm. (It was necessary to use 4/9 polyvinyl chloride and 5/9 dioctyl

adipate in this case to attain sufficient fluidity.)

Review of these results showed no effect on high-pressure burning except for the largest filament size (660-micron) at the higher pressure. To learn more about the nature of this effect, a new set of data were obtained with 1000-micron (1-mm) holes in 4x4 mm strands. Burning-rate results were very erratic, some strands burning twice as fast as others. The slower-burning specimens gave points falling on the matrix burning-rate curve. It was concluded that the occasional high-burning-rate results when large holes were present was due to occasional cracking or spalling of the specimens by thermal shock, the effect being aggravated by the large drilled hole. Except for this effect, it appears that polymer columns of 340 to 1000 microns diameter do not influence burning rate at least at pressures above 20 atm.

Since in actual propellants the pockets of fuel between particles may have dimensions such as microns or tens of microns rather than hundreds of microns, further experiments were performed in which a 38-micron filament of rayon was surrounded by ammonium perchlorate powder which was then pressed to form a strand around the filament. Two such strands, burned at 48 atm, had measured rates of 0.62 and 0.71 cm/sec respectively. The pure ammonium perchlorate rate at this pressure is 0.60 cm/sec. Thus no large acceleration was produced by the filament. (By contrast, a copper filament embedded in a propellant may produce a several-fold increase in propagation rate.)

E. Experiments with Potassium Perchlorate Pressed Strands

Other experiments have been performed with strands pressed from potassium perchlorate (not a monopropellant) instead of ammonium perchlorate. Experiments with such strands and a methane flame show that the flame becomes colored violet, indicating potassium vaporization and corresponding oxygen release, as expected, but simultaneous melting and bubbling of the potassium perchlorate occurs. Also, cracks induced by thermal stress appear in the unmelted portion of the strand. These effects made experiments with controlled geometry impossible, so this approach was not continued.

IV. REVIEW OF PRESENT KNOWLEDGE OF COMBUSTION MECHANISM OF AMMONIUM PERCHLORATE-BASED COMPOSITE SOLID PROPELLANTS

This discussion will be limited to the mechanism of steady-state burning of ammonium perchlorate-based solid propellants, and will not consider the mechanisms of ignition, erosive burning, or combustion-acoustic interactions leading to instability. Also, composite propellants with metallic ingredients such as aluminum will not be considered here, largely because little basic research reported in the unclassified literature has been devoted to this problem.

With the problem thus limited, it turns out that only a very small number of research teams have made significant contributions. In addition to our own work (1, 2, 3, 4, 5), one may list the contributions of Schultz, Chaiken, Andersen, and co-workers at Aerojet-General Corporation (11, 14, 15, 16), of Summerfield and co-workers at Princeton (7, 17, 18, 19, 20) of Adams and co-workers in England (6, 21, 22), and a related group of theoretical studies by Nachbar, Penner, Spalding, Williams, et al. at Lockheed and at California Institute of Technology (23, 24, 25, 26, 27).

Our main interest is in understanding what controls the burning rate and its variation with pressure, composition, etc. The most important experimental findings relevant to the burning mechanism, drawn from the entire above body of work, will be listed.

(1) For a mixture of ammonium perchlorate crystals dispersed in an organic fuel matrix, the burning rate, of the order of one cm/sec at 70 atm, generally increases with increasing pressure, increasing fineness of crystal size, and increasing ratio of oxidizer to fuel (practical mixtures are always on the fuel-rich side of stoichiometric).

(2) The variation of burning rate with the above parameters is complex. For example, for a rather fuel-rich mixture, the burning rate increases much more rapidly with increasing fineness of grind at low pressures (1-10 atm) than at high pressures (50-100 atm).

(3) Temperature measurements show that the flame zone above the propellant surface at high pressure must be extremely thin, of the order of microns or

tens of microns. This is consistent with a calculation of the necessary high temperature gradient which must exist to vaporize the solid at a rate of one cm/sec during burning at elevated pressure. Both experiments and calculations show that radiant transfer makes at most a second-order contribution to the heat transfer from flame gases to solid surface.

(4) Examination of a rapidly quenched propellant surface shows dramatic differences depending on the combustion pressure. At low pressure (1-10 atm), the oxidizer crystals project above the fuel surface, while at high pressure (50-100 atm) fuel filaments project upward and oxidizer crystals are found at the bottom of holes in the surface.

(5) Pure ammonium perchlorate, when dead-pressed into a strandlike shape, can be ignited at pressures above about 22 atm. A flame propagates with a burning rate which increases with increasing pressure, being one cm/sec at 102 atm. Pure ammonium perchlorate will propagate a flame even at one atmosphere if a sufficient incident radiant flux is supplied ($10 \text{ cal/cm}^2\text{-sec}$) or if the ammonium perchlorate is preheated to about 280°C before ignition.

(6) Replacement of ammonium perchlorate in a propellant composition by another oxidizer such as ammonium nitrate or potassium perchlorate will cause large changes in burning rate.

In view of these findings, Bastress, Hall, and Summerfield (7) have proposed that three regimes must be considered. At high pressures, the ammonium perchlorate decomposition flame apparently propagates fast enough to be rate-controlling, and the burning rate is about equal to the pure ammonium perchlorate rate and is insensitive to particle size. At somewhat lower pressures, a granular diffusion flame becomes governing, the rate-controlling steps being the rate of mixing of fuel and oxidizer vapors and the rate of energy feedback to the condensed-phase ingredients. In this regime, particle size is important because it is presumably related to the characteristic size of pockets of gaseous reactant. Finally, at extremely low pressures and/or for extremely fine particle size, diffusional mixing will become rapid relative to gaseous chemical reaction rates, and the problem reduces to that of a pre-mixed gaseous flame with a heat sink at the cold boundary. In this regime, burning rate would be independent of particle size.

In practice, overlapping of these regions will be expected. The problem is even more complex because practical propellants use bimodal particle-size distributions to improve the fluidity of the mix and permit achievement of higher solids loadings and hence hotter flames. However, the qualitative features seem reasonable.

Theoretical analysis of the postulated regime dominant at the lowest pressures, where the premixed gaseous flame is governing, is relatively straightforward and can be carried out in terms of one-dimensional gaseous flame theory with a suitable cold-boundary condition. The kinetics of the gaseous reaction of interest would be approximated by those of the familiar hydrocarbon-oxygen premixed flame, perhaps modified by the nitric oxide which will constitute part of the oxidizer. From the pressure dependence of burning velocity of such gaseous flames, we know that the overall reaction rate is nearly second-order, and can accordingly show that the solid propellant burning rate in this regime should be directly proportional to pressure. If the model is modified by including a surface-temperature-dependent pyrolysis rate which is coupled to the gaseous flame rate, then the burning rate will come out to vary less than linearly with pressure even for a second-order reaction (because at higher pressures and corresponding thinner reaction zones there will be more back-diffusion of products into reactants and corresponding dilution leading to decrease of volumetric gaseous reaction rate); such a variation agrees with the experimental trend. However, there seems to be a problem in regard to the absolute magnitude of the burning rate in this regime. Bastress et al. (7) quote a burning rate at one atm of 0.15 cm/sec for a finely ground propellant with adiabatic flame temperature of 2240°K. This corresponds to a mass consumption rate of about 0.22 gm/cm²-sec. However, a stoichiometric hydrocarbon-air flame of about this flame temperature would have a burning rate of only about 35 cm/sec or 0.042 gm/cm²-sec, which is less than one-fifth the rate of the solid propellant, even though the cold-boundary heat sink would tend to decrease the solid-propellant rate. Possibly the pyrolysis gases contain significant proportions of hydrogen or other constituents which would tend to increase the flame speed; certainly the final products are rich in hydrogen, and the resulting increase in thermal conductivity

in the gaseous reaction zone will increase burning rate. Nonetheless the fivefold increase over a hydrocarbon-air premixed flame seems larger than would be expected.

Theoretical analysis of the intermediate regime, the granular diffusion flame, has been made by Summerfield et al. (7, 18) with the use of arbitrary simplifying approximations. Gas pockets in the flame are assumed to be spherical with a radius proportional to the oxidizer particle size. Equal expansion in both transverse and normal directions is assumed, so that the gaseous sphere is larger than the original solid particle by the cube root of the ratio of specific volumes. The burning rate is then found to vary directly with the cube root of pressure and inversely with the first power of particle diameter. If, instead of this model, a two-dimensional model is considered in which gas expansion occurs only in the normal direction and not transversely, the burning rate is easily shown to be independent of pressure. Nachbar (25) has formulated a treatment of such model. The actual behavior is presumably somewhere between these extremes and is extremely difficult to describe theoretically even when the fuel-oxidizer chemical reaction is taken to be infinitely fast and the decomposition flame of the ammonium perchlorate crystals is neglected, because of the complex geometry and unsteady-state nature of the process. It is even possible (7) that turbulence is important in the mixing process in the case of large oxidizer crystals, the turbulence being triggered by the non-steady flow from the surface, with gas-pocket breakup occurring when the Reynolds number exceeds about twenty. However, there seems to be no direct evidence yet for this latter mechanism.

To summarize, the granular diffusion flame concept provides a convenient and logical picture for the transition region between the fuel-oxidizer premixed flame which must govern at sufficiently low pressures and oxidizer sizes and the ammonium perchlorate decomposition flame which is apparently of critical importance at high pressures and any oxidizer size. However, no rigorous mathematical theory of this granular diffusion flame is available, and even if it were, this theory would then have to be merged with the contributions from the regimes on either side.

At relatively high pressure, various types of evidence already mentioned indicate that the monopropellant decomposition flame burning on each ammonium perchlorate crystal becomes dominant as a rate-controlling mechanism. The most important argument is that the decomposition-flame burning rate increases more rapidly with pressure than the propellant burning rate, and the curves essentially come together at around 100 atm (cf. Fig. 9 of ref. (7)), in spite of the final temperature of the propellant flame being 1000°K higher than that of the perchlorate decomposition flame. Further confirmatory evidence comes from the relative insensitivity of propellant burning rate to particle size at high pressure and large binder content. Again, the appearance of the quenched surface after high-pressure combustion has been described as showing binder filaments projecting up and oxidizer crystals at the bottom of depressions in the surface, which would be expected if the decomposition flame is controlling. Finally, it is generally true that propellant burning rates are relatively sensitive to changes in the oxidizer chemistry, particularly changes affecting decomposition kinetics, and are relatively insensitive to changes in polymer type or properties. Thus, a strong case exists for believing the ammonium perchlorate decomposition flame dominates the composite propellant burning process at high pressures and significantly influences it even at lower pressures.

On the other hand, it is unreasonable to expect no interaction between the fuel-oxidizer diffusion flame and the oxidizer decomposition flame even at high pressures. The binder properties and the fuel-oxidizer interdiffusion will always make some contribution to combustion behavior, by a mechanism involving additional energy feedback to the oxidizer crystals. Chaiken and Andersen (15) have discussed the details of such interactions. However, quantitative treatment of this problem is obviously difficult because of the complex geometry and unsteady-state nature of the burning, and in any case is premature until the unperturbed oxidizer decomposition flame is thoroughly understood.

Let us consider what is known about ammonium perchlorate burning as a monopropellant. The salient feature of this process have been described

by Levy and Friedman (4).

At normal ambient temperatures, ammonium perchlorate which is dead-pressed in the form of a strand can be ignited at pressures above 22 atm. The burning rate increases with pressure, (Figure 1, ref. (4)). Combustion may be induced at lower pressures by preheating the strand, or providing a sufficient incident radiant flux during burning, but not by using larger samples. The lower pressure limit has been postulated (4) as due to radiant heat loss to the surroundings; detailed theoretical examination of this postulate by Nachbar and Johnson (23) show that it is qualitatively reasonable but requires assumption of a larger rate of energy loss from the system than can plausibly be accounted for by radiation. In view of the complexity of Nachbar and Johnson's calculations, the writers can only comment that no alternate reasonable explanation of the deflagration limit seems available.

The ammonium perchlorate steady-state deflagration appears to involve the gas phase, because: (a) it is easily shown that sublimation occurs when ammonium perchlorate is heated in vacuum; (b) the deflagration rate is quite pressure-dependent. It is logical to postulate that gaseous species such as ammonia and perchloric acid vapor react rapidly in a gaseous zone just above the crystal surface, with energy feedback from exothermic gaseous reactions to the crystal. (It is of interest to note that ammonium perchlorate does not melt even if heated to just below the auto-ignition temperature at several hundred atmospheres. If it is heated in a small sealed ampoule, it will dissolve in its decomposition products, of which water is a prominent constituent.)

If we accept the premise that the major source of exothermic reaction in the flame is a gaseous redox reaction just above a crystalline surface, we have thus identified two important rate processes, the overall rate of this reaction and the rate of energy feedback to the crystal, which when coupled will determine a burning rate. The possibility remains, however, that the vaporization of the crystal is itself a rate process rather than an equilibrium process.

Equilibrium would exist between solid and vapor if sufficient time were available, the rate of condensation being nearly as large as the rate of vaporization, and the net rate of volatilization being determined by the rate of heat supply to the surface. If insufficient time were available, relative to the absolute evaporation rate, then that rate would be limiting at the prevailing surface temperature, which again is governed by a heat balance. Thus, we do not know if an equilibrium or kinetic process is occurring at the surface. The problem has been discussed in references (3) and (26).

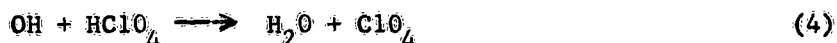
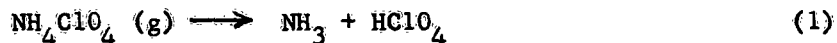
The types of experimental information which would help in understanding the surface process are: (a) measurements of vapor pressure, heat of vaporization, and degree of association in the gas phase of ammonium perchlorate; (b) accommodation coefficients of the gaseous species on the surface; and (c) surface-temperature measurements for burning ammonium perchlorate. Information of types (a) and (b) are not available, because of difficulties of such measurements in chemically unstable systems. As for the surface temperature, while no accurate values are available, photopyrometric measurements of the burning surface at 500 psi indicated a temperature of the order of 1000-1100°K (3); the exact value would depend on the unknown emissivity of the surface. The Aerojet hot-plate pyrolysis technique (14, 16), if valid, gives surface temperature vs pyrolysis rate over a range of preignition conditions; temperatures as high as 900°K (at 0.13 cm/sec) were measured, the apparent activation energy being 22 kcal. However, there is an important question as to whether the hot-plate temperature is the same as the oxidizer surface temperature, or whether gradients exist (26).

Another aspect of the vaporization process which requires consideration is the inhomogeneous nature of the crystalline ammonium perchlorate and the complex mode of decomposition which is observed at relatively low temperatures. Apparently a portion of the crystal decomposes rather readily (about 30 per cent of the starting material), leaving a porous residue which is much more stable to decomposition (28). The material which decomposes first may be intermosaic matter, or imperfect crystals, in spaces between perfect crystals which are more stable. A further observation is that low-temperature

decomposition appears to initiate at specific sites on the surface and then spreads over the surface as a visible interface. The nature of these processes seems to be different in the so-called low-temperature range (220-350°C) discussed above and the "high-temperature" range (350-440°C), as studied by several investigators (29, 30). In the 350-440°C range, under vacuum conditions, sublimation without decomposition is the dominant process. Sublimation may be "suppressed" by providing a sufficient pressure of inert gas, and then decomposition occurs with a much higher activation energy than in the low-temperature region, and also decomposition goes to completion rather than stopping at 30%. Presumably the heat-generating reactions occurring here are gaseous (29). Rate may be governed by desorption (11), by proton-transfer (30), or by breakdown of the perchlorate ion (29). The relation between these decomposition studies, the hot-plate pyrolysis experiments, and the high-pressure or radiation-assisted deflagration is not clear at the present time. This makes it impossible to provide a soundly based theoretical relationship between the surface temperature of deflagrating ammonium perchlorate and the propagation rate.

Another important aspect of ammonium perchlorate deflagration is the non-equilibrium nature of the combustion products, as revealed by product-temperature measurements (1) and product-gas analysis (4). The theoretical final temperature of pure crystalline ammonium perchlorate initially at 25°C reacting adiabatically at a constant pressure of 100 atm to give products in chemical equilibrium comes out to be 1440°K, while the measured temperature at this pressure is only 1203°K. The products at equilibrium should consist mainly of H_2O , O_2 , N_2 , and HCl , the theoretical molecular ratios of Cl_2/HCl and NO/N_2 being 0.11 and 0.004 respectively. Product analysis at 100 atm indicates a NO/N_2 ratio of 0.6 to 0.8 instead of 0.004. Thermo-chemical calculations show this result to be generally consistent with the low flame temperature, the decomposition of nitric oxide to its elements being exothermic. The fraction of oxygen remaining oxidized to the nitric oxide stage was found to be pressure-dependent, decreasing as pressure is increased from one atm to 68 atm, but not changing further on additional pressure increase to 136 atm. Flame-temperature measurements were not precise enough to show whether the temperature increased with increasing pressure.

Speculation about the kinetics of the gaseous oxidation-reduction reactions above the ammonium perchlorate surface may be found in the literature (4, 30). Various of the following gaseous reactions may be of significance:



The rate of reaction (2) above, controlling the decomposition of perchloric acid vapor, is believed to be known from kinetic measurements reported by Levy (5). It is of interest to know if this reaction could possibly be controlling in the flame, or whether its rate is too slow. It is also generally of interest to know the order of magnitude of the overall reaction rate in the gaseous flame which is compatible with observed burning rate vs pressure data. The requisite mathematical techniques for approaching this problem have been developed by Nachbar and Johnson (23). However, the results are not expressible in a form which is convenient for algebraic manipulation, so the present investigators have derived some very simple approximate relationships which take into account all the rate processes in the Nachbar-Johnson treatment but which make gross mathematical approximations. The results are believed to give correct trends and orders of magnitude, but obviously should be repeated on the more rigorous basis if quantitative conclusions are to be drawn.

The model and equations are described in Appendix I. Briefly, a one-dimensional steady-state propagation is assumed. Energy is generated in

a gaseous reaction of arbitrary order n , pre-exponential factor A , and activation energy E . Heat is conducted back to a solid-gas interface at temperature T_s where exothermic vaporization occurs at a rate assumed to be given by the relation

$$r = 31 T_s \exp (-22,000/RT_s)$$

which was obtained by hot-plate pyrolysis studies. (In view of the uncertainty in this relation, discussed above, the whole treatment is of questionable value, but may be useful in showing the relationship between various possible values of the parameters.) In addition to the foregoing three rate processes (exothermic gaseous reaction, heat transfer, endothermic surface reaction) a fourth rate process, interdiffusion of products and reactants in the gaseous reaction zone, is included. This last process leads to dilution of the reactants and reduction of the volumetric rate of heat release, the magnitude of the effect varying with pressure. The Lewis number is taken as unity, and other simplifications are made, as stated in the Appendix.

Then, by requiring the solution to pass through the experimental point ($r = 1$ cm/sec, $P = 102$ atm, $T_u = 294^\circ\text{K}$), it is possible to determine the relationship of r to P for any assumed value of reaction order n . This has been done for first-order and second-order kinetics. The result is independent of gaseous activation energy E , since the flame temperature is taken as independent of pressure. Second-order kinetics is found to fit the experimental data more closely than first-order kinetics.

If one then substitutes reasonable numerical values for all known parameters, one may calculate the required values of gaseous kinetic constants to give agreement between measured and calculated rates. When first-order kinetics is assumed, the required constant comes out to be $1 \times 10^8 \text{ sec}^{-1}$. This may be compared with the value $3.7 \times 10^5 \text{ sec}^{-1}$ extrapolated from lower-temperature measurements of perchloric acid vapor decomposition rates (5). Obviously this reaction is much too slow to be determining the flame speed. The results could be accounted for by assuming a chain length of several hundred resulting

from each decomposing HClO_4 molecule. However, since many radicals, such as OH , NH_2 , etc., are presumably always present in the flame in substantial concentrations, it seems likely that additional radicals contributed by HClO_4 breakdown are not of significant importance.

When second-order kinetics is assumed, the overall apparent rate constant is $4 \times 10^{12} \text{ cm}^3/\text{mole-sec}$. This may be compared with a typical pre-exponential factor at the prevailing flame temperature, calculated from simple collision theory as roughly $3 \times 10^{14} \text{ cm}^3/\text{mole-sec}$. Then, $\exp(-E/RT)$ would have to be $4 \times 10^{12} / 3 \times 10^{14} = 0.013$ and $E = 10.5 \text{ kcal/mole}$. This seems generally reasonable for a radical reaction.

The actual gaseous activation energy can in principle be calculated from measurements of burning rate vs initial temperature if the corresponding variation of final temperature is known.

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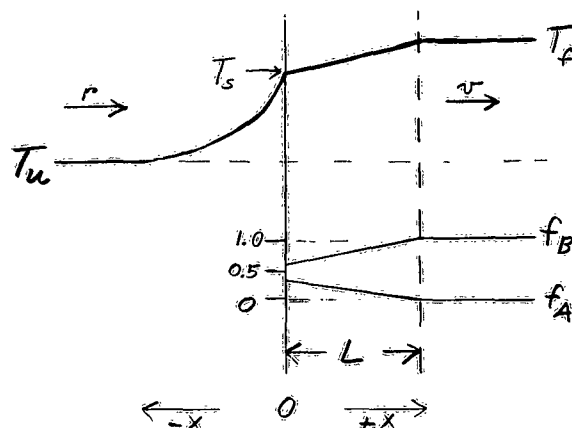
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APPENDIX A

Simplified Equations for Monopropellant Combustion

Symbols:

A	pre-exponential factor in gaseous reaction rate law ($\text{gm cm}^{-3} \text{ atm}^{-2} \text{ sec}^{-1}$) or ($\text{gm cm}^{-3} \text{ atm}^{-1} \text{ sec}^{-1}$) depending on reaction order
C_g	specific heat of gas at constant pressure ($\text{cal/gm}^\circ\text{C}$)
C_s	specific heat of solid at constant pressure ($\text{cal/gm}^\circ\text{C}$)
D	diffusion coefficient of product into reactant (cm^2/sec)
E	activation energy of gas reaction (cal/mole)
f_A	mass fraction of reactant in gas
f_B	mass fraction of product in gas
ΔH	heat of gaseous reaction (cal/gm)
K	gaseous reaction rate ($\text{cal/cm}^3\text{-sec}$)
L	thickness of gaseous reaction zone (cm)
P	pressure (atm)
Q	heat of gasification of solid (cal/gm)
R	gas constant ($\text{cal/mole}^\circ\text{K}$)
r	regression rate of solid (cm/sec)
T_f	flame temperature ($^\circ\text{K}$)
T_s	surface temperature ($^\circ\text{K}$)
T_u	unburned solid temperature ($^\circ\text{K}$)
\bar{T}	effective temperature in gaseous reaction zone ($^\circ\text{K}$)
W	gaseous reaction rate ($\text{gm/cm}^3\text{-sec}$)
v	gas velocity (cm/sec)
x	distance coordinate (cm)
λ	thermal conductivity of gas ($\text{cal/cm-sec}^\circ\text{C}$)
ρ	gas density (gm/cm^3)
ρ_s	density of solid (gm/cm^3)



Steady-state propagation is assumed. For x less than zero, the solid heats from T_u to T_s , the surface temperature at $x = 0$. At the surface, vaporization occurs endothermically, absorbing Q cal/gm. The rate of vaporization r is related to T_s by the relation

$$r = 31 T_s \exp(-22,000/RT_s) \quad (1)$$

determined by Aerojet with the hot-plate pyrolysis technique (Andersen and Chaiken, ARS Jour. 31, 1379 (1961)). Above the surface is a gaseous reaction zone of thickness L , in which gaseous reactant A is converted into product B by a second-order reaction evolving ΔH cal/gm. Temperature and concentration gradients in this zone are arbitrarily assumed to be linear, as an approximation. Interdiffusion of product and reactant is permitted. Final temperature is T_f . The gaseous reaction rate K (in thermal units) or W (in mass units) per unit volume of flame, in the region $0 < x < L$, is assumed to be governed by the relation

$$W = K/\Delta H = A (\bar{f}_A \bar{P})^n \exp(-E/\bar{R}\bar{T}) \quad (2)$$

where \bar{f}_A and \bar{T} are effective values of f_A and T in the reaction zone.

Basic Equations:

A balance of heat flow from gas to solid gives

$$\lambda (T_f - T_s)/L = [Q + c_s (T_s - T_u)] r \rho_s \quad (3)$$

An overall energy balance gives

$$KL = r\rho_s \Delta H \quad (4)$$

From continuity,

$$r\rho_s = v\rho \quad (5)$$

From a balance on species B in the gaseous reaction zone, the chemical generation term being neglected,

$$D\rho (1 - f_{BS})/L = v\rho f_B \approx v\rho \quad (6)$$

By rearrangement of Equation (6), and noting that $f_A = 1 - f_B$,

$$f_{AS} = vL/D \quad (7)$$

It will be assumed that $\bar{f}_A = f_{AS}/2$, so that

$$\bar{f}_A = vL/2D \quad (8)$$

Finally, the Lewis number is taken as unity:

$$\lambda = C_g \rho D \quad (9)$$

Working Equations Describing the Flame:

The following relations follow from the foregoing equations:

$$r = \frac{1}{\rho_s} \sqrt{\lambda(T_f - T_s) W [Q + C_s (T_s - T_u)]} \quad (10)$$

$$W = A (\bar{f}_A P)^n \exp (-E/RT) \quad (2)$$

$$\bar{f}_A = \frac{C_g (T_f - T_s)}{2 [Q + C_s (T_s - T_u)]}$$

$$L = \sqrt{\frac{\lambda (T_f - T_s)}{W [Q + C_s (T_s - T_u)]}} \quad (12)$$

By combining (2), (10), and (11),

$$r = \frac{1}{\rho_s} \sqrt[n]{\frac{\lambda A C_g^n (T_f - T_s)^{n+1} P^n \exp(-E/R\bar{T})}{2^n [Q + C_s (T_s - T_u)]^{n+1}}} \quad (13)$$

or, if ρ_s , λ , A , and C_g are taken to be independent of P and T_u ,

$$r = B \left[\frac{T_f - T_s}{Q + C_s (T_s - T_u)} \right]^{\frac{n+1}{2}} P^{n/2} \exp(-E/2R\bar{T}) \quad (14)$$

$$\text{where } B = \frac{1}{\rho_s} \sqrt[n]{\frac{\lambda A C_g^n}{2^n}} = \text{constant} \quad (15)$$

Numerical values:

$$\lambda = 1.6 \times 10^{-4} \text{ cal/cm-sec-}^\circ\text{C}$$

$$C_g = 0.32 \text{ cal/gm-}^\circ\text{C}$$

$$C_s = 0.264 \text{ cal/gm-}^\circ\text{C}$$

$$Q = 477 \text{ cal/gm}$$

$$\rho_s = 1.95 \text{ gm/cm}^3$$

$$R = 1.987 \text{ cal/mole-}^\circ\text{K}$$

$$\text{Then } B = 2.08 \times 10^{-3} \sqrt[n]{A/2^n} \quad (16)$$

To obtain E , the following equation is obtained from (14) if a pair of values of $r(P, T_u)$ are known such that \bar{T} is different in the two cases, designated 1 and 2:

$$E = \frac{R \bar{T}_1 \bar{T}_2}{\bar{T}_2 - \bar{T}_1} \ln \left\{ \left[\frac{(T_{f1} - T_{s1}) [Q + C_s (T_{s2} - T_{u2})]}{(T_{f2} - T_{s2}) [Q + C_s (T_{s1} - T_{u1})]} \right]^{n+1} \left(\frac{r_2}{r_1} \right)^2 \left(\frac{P_1}{P_2} \right)^n \right\} \quad (17)$$

From the pair of values

$$P = 102 \text{ atm}, T_u = 294^\circ\text{K}, r = 1 \text{ cm/sec}$$

$$\text{and } P = 57 \text{ atm}, T_u = 343^\circ\text{K}, r = 1 \text{ cm/sec}$$

one may solve for E. We take $\bar{T} = T_f$, and calculate T_f from

$$T_f = 1203 + 0.813 (T_u - 294)$$

We obtain T_s from equation (1). When $n = 2$, (second-order reaction) we obtain $E = 25,400 \text{ cal/mole}$. When $n = 1$, $E = 2,200 \text{ cal/mole}$ (first-order reaction). These values may not be meaningful because Equation (18) may not be an acceptable way to calculate T_f , it being known that the flame does not burn to give equilibrium products.

Shape of r vs P curves:

Let us require that the curve pass through $r = 1 \text{ cm/sec}$, $P = 102 \text{ atm}$, $T_u = 294^\circ\text{K}$. Then, if \bar{T} is independent of P, and taking T_s from Equation (1), it follows from Equation (14) that

$$r = \frac{(4.94)^{(n+1)/2}}{102^{n/2}} \left[\frac{1203 - T_s}{400 + 0.264T_s} \right]^{\frac{n+1}{2}} P^{n/2} \quad (18)$$

For second-order reaction (for any activation energy E),

$$P = 9.3r \left[\frac{400 + 0.264T_s}{1203 - T_s} \right]^{3/2} \text{ atm} \quad (19)$$

For first-order reaction (for any activation energy E),

$$P = 4.19 r^2 \left[\frac{400 + 0.264T_s}{1203 - T_s} \right]^2 \text{ atm} \quad (20)$$

These equations are plotted in Figure A-1. It is seen that the second-order curve agrees more closely with experiment.

Required Values of Kinetic Constants

Appropriate first-order and second-order kinetic constants may be calculated to be consistent with equations (19) and (20) and the other equations

leading up to it.

When first-order is assumed, the value of k then comes out to be $9.7 \times 10^7 \text{ sec}^{-1}$, to be in agreement with the observed burning rate. (This may be compared with $3.7 \times 10^5 \text{ sec}^{-1}$ for the perchloric acid rate constant extrapolated to flame temperature.)

When second-order is assumed, the required rate constant comes out to be $3.65 \times 10^{12} \text{ cm}^3/\text{mole-sec}$. A "collision number," or pre-exponential factor, can be computed by assuming an activation energy. Upon assuming 25,400 cal/mole for E , the collision number comes out as $1.5 \times 10^{17} \text{ cm}^3/\text{mole-sec}$. A typical theoretical collision number at 1200°K, assuming $\sigma = 4 \times 10^{-8} \text{ cm}$ and reduced mass = 30, and no steric effects, is $2.8 \times 10^{14} \text{ cm}^3/\text{mole-sec}$. When this theoretical collision number is used, E then would have to be 10,500 cal/mole.

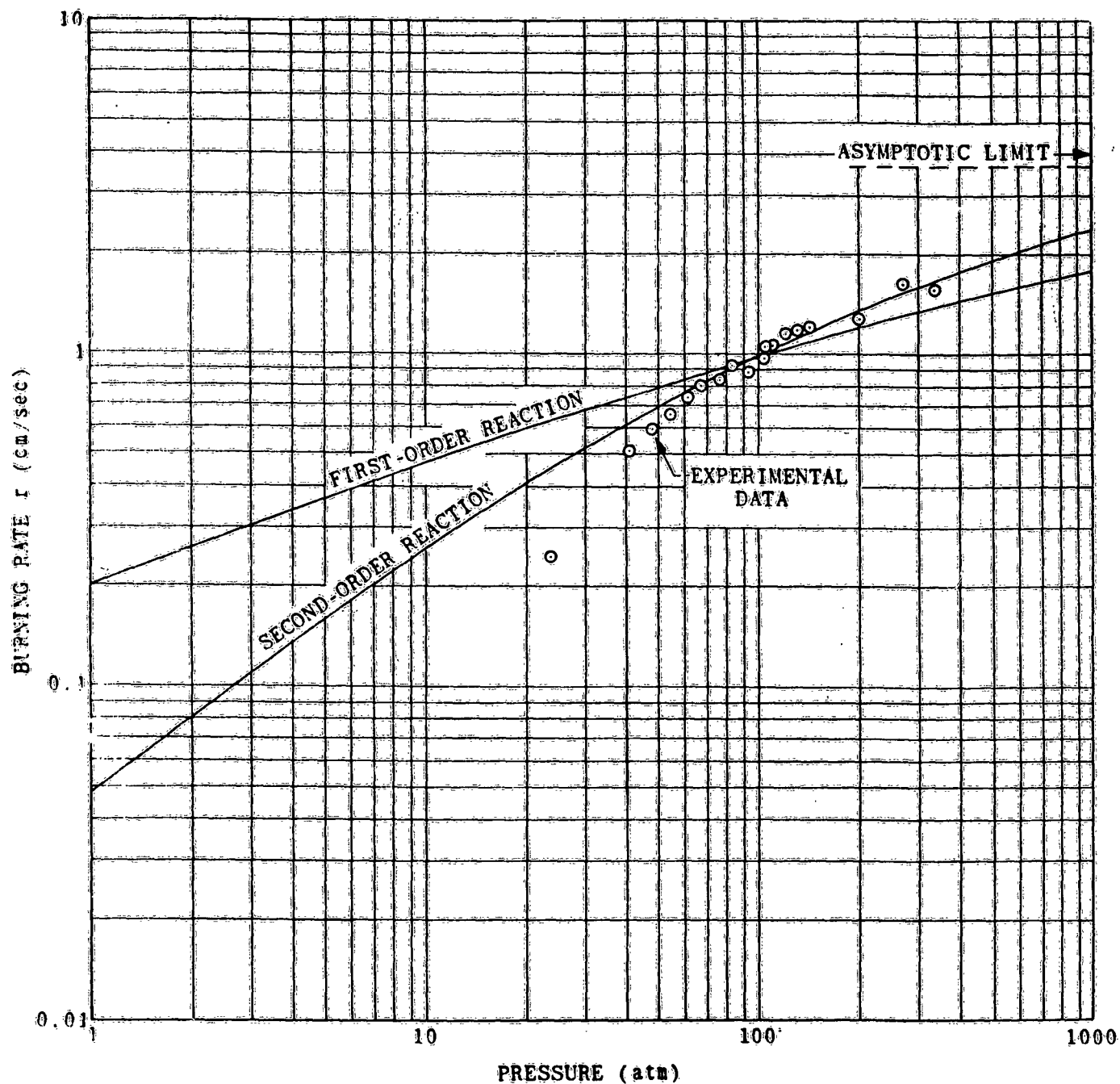


Figure A-1. CALCULATED BURNING-RATE VERSUS PRESSURE CURVES FOR ASSUMED FIRST AND SECOND ORDER GAS-PHASE KINETIC LAWS.